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A FACILE ROUTE TO BICYCLO[3.3.0]OCTANES THROUGH CLEAN TRANSANNULAR CYCLISATION OF 1-TRIMETHYLSILYLCYCLOOCTENE UNDER FRIEDEL-CRAFTS CONDITION

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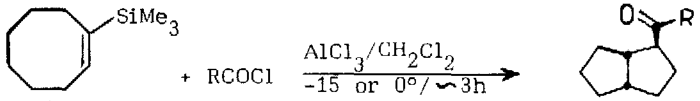
Abstract: *A wide range of exo-cis-bicyclo[3.3.0]-2-octyl ketones are obtained by the reaction of 1-trimethylsilylcyclooctene with various acyl chlorides in presence of aluminium chloride.*

The reaction of cyclooctene with acetyl chloride in presence of aluminium chloride leads to a mixture of several products even under carefully manipulated conditions.[1] We have now found that the presence of silicon on the vinylic position[2] favourably alters the status of this reaction with the result that 1-trimethylsilylcyclooctene (**1**) undergoes clean transannular cyclisation reaction with various acyl chlorides to give exo,cis-bicyclo[3.3.0]-2-octyl ketones, **2–9**,[3] (Scheme I). The results are summarised in the Table.

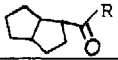
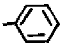


1 **2–9**

Scheme I

As **1** can be prepared conveniently,[4] this reaction offers a valuable route to the bicyclo[3.3.0]octane moiety which forms part of a number of important classes of compounds, and currently five-membered carbocycles in general are focus of much research.[5]

TABLE : Acylation of 1-trimethylsilylcyclooctene to bicyclo[3.3.0]-2-octyl ketones (**2-9**).

	R	Yield (%)^b	B.P.(°C/Torr)^c
2	$-CH_3$	71	50 - 52/0.5
3	$-CH_2-CH_3$	61	63 - 65/0.6
4	$-CH_2-CH_2-CH_3$	60	80 - 82/0.5
5	$-\underset{CH_3}{CH}-CH_3$	56	69 - 70/0.5
6	$-(CH_2)_{10}-CH_3$	57	150-155/0.4
7		63	120-121/0.8
8	$-CH_2-$	65	143-145/0.9
9	-CH=CH-	60	135-139/0.5

(**a**) The products were identified by their NMR, IR and MS data and by derivatives wherever possible. (**b**) Yields are of distilled products of >95% purity by GC. (**c**) Boiling points are uncorrected.

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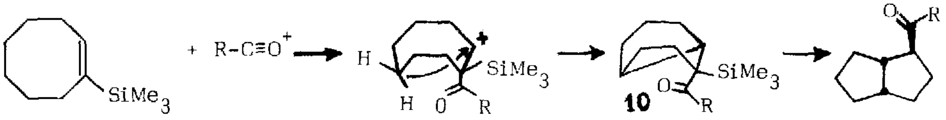
In the acid-catalysed ring opening of the epoxide of 1[6] and in bromination of 1,[7] transannular nucleophilic attack by C_5-H bond on C_1(α-carbon) was observed. In the present case, the α-carbon is likely to be attacked by the electrophilic acyl carbon generating a positive charge on C_2 that would be stabilised by silicon (β -effect)[2,8] which confers a longer lifetime on the intermediate β -silyl cation, relative to that of the simple cyclooctene. This enables smooth C_2-C_6 bond formation by otherwise presumably entropically unfavourable transannular deprotonation to give the observed products. We have found that the acyl groups in **2** and **7** occupy the exo position,[9] and presumably the other products also possess the same geometry. The reaction path could possibly be depicted as in Scheme II. The easy loss of the silyl group α to the keto group in **10** by way of an enol followed by the thermodynamically controlled C-protonation of the enol is the possible route to the observed stereochemistry.[11]



Scheme II

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3. Brief experimental procedure: Trimethylsilylcyclooctene (**1**) (3 mmol) in CH_2Cl_2 (60 mL) is added dropwise (3 h) to a mixture of the desired acyl chloride (6 mmol) and anhydrous $AlCl_3$ (9 mmol) in CH_2Cl_2 (20 mL) kept stirred at -15 to 0° under nitrogen. After stirring for 10 min more, the mixture is worked up in the usual way and the product distilled.

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9. The compounds **2** and **7** are reported in the literature.[10] Their characteristics and those of their derivatives are same as those reported in the literature.[10] **3** is mentioned in ref. 10(c), but no properties are given.

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11. The authors are grateful to the referee for this suggestion.

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